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(54) Title: **A HALOPYRROLE LIGAND FOR USE IN A CATALYST SYSTEM**

(57) Abstract: A pyrrole ligand for an olefin oligomerisation catalyst system wherein the pyrrole ligand incorporates a halogen source and wherein the ligand is a halopyrrole or a derivative thereof. The halopyrrole may be a halopyrrole-containing compound. The halopyrrole-containing compound of the present invention is any pyrrole derivative of general formula $X-(CH_2)_n-C_4H_4N$, where X can be a halide selected from the group consisting of fluoride, chloride, bromide and/or iodide, and n can be any number greater than 0. Typical halopyrrole-containing compounds of the invention have from about 4 to about 20 carbon atoms per molecule. The halopyrrole-containing compounds include derivatives of pyrrole having a bromoalkyl group bonded to the pyrrole ring.

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A HALOPYRROLE LIGAND FOR USE IN A CATALYST SYSTEM

5 **Field of the Invention**

This invention relates to a halopyrrole derived ligand for use in a catalyst system for hydrocarbon conversion and to a catalyst system including a halopyrrole derived ligand for use in a hydrocarbon conversion process. The invention
10 further provides a halopyrrole derived ligand and a catalyst system for the oligomerisation of olefins, for example ethylene.

Background to the Invention

15 The oligomerisation of olefins, primarily α -olefins, with chromium catalysts has been extensively studied. More specifically, a number of chromium catalysts have been developed and used to trimerize olefins. In this regard, the trimerisation of ethylene to 1-hexene is significant since, in addition to its use as a specific chemical, 1-hexene is extensively used in polymerization processes
20 either as a monomer or comonomer.

Furthermore, the trimeric products derived from longer chain olefins could be well utilized as synthetic lubricants (e.g. polyalphaolefins / PAOs), as well as various other applications such as drilling muds, and as feedstock to prepare detergents
25 and plasticizers.

Known chromium-based processes for the trimerisation of ethylene to 1-hexene include:

- 5 a) A process in which olefins are trimerised by passing the olefin in contact with a catalyst comprising the reaction product of a chromium compound, an organoaluminium compound hydrolyzed with a specific amount of water and a donor ligand selected from hydrocarbyl isonitriles, amines and ethers (US Patent No. 4,668,838);
- 10 b) Trimerization of olefins by chromium-containing compounds, such as, for example, chromium pyrrolides that are prepared by forming a mixture of a chromium salt, a metal amide and an electron pair donor solvent, such as, for example, an ether. These chromium catalysts can be used either unsupported or supported on an inorganic oxide (European Patent No. 0 416 304);
- 15 c) A process to trimerise ethylene to 1-hexene comprising contacting ethylene with a stabilized catalyst system comprising a chromium source, a pyrrole-containing compound, a metal alkyl and an aromatic compound (European Patent No. 0 668 105);
- 20 d) A process for preparing an α -olefin oligomer which comprises oligomerising an α -olefin in a saturated hydrocarbon solvent in the presence of a chromium-based catalyst system comprising a combination of at least a chromium compound, an amine or metal amide, an alkylaluminium compound and a non-coordinating Lewis acid-containing compound based on an element
25 selected from groups IIIB, IVB, VB and VIB of the periodic table (European Patent No. 0 706 983);

- e) A process for producing 1-hexene which comprises trimerising ethylene in a 1-hexene solvent in the presence of a catalyst system obtainable by contacting in a 1-hexene solvent a chromium-containing compound, trialkylaluminium or dialkylaluminium hydride, a pyrrole compound or derivative thereof and a group 13 (III B) or group 14 (IV B) halogen compound (European Patent No. 0 699 648);
- f) A process for the trimerisation of ethylene, said process comprising reacting ethylene, using a catalyst comprising an aluminoxane and a polydentate phosphine, arsenic and/or stibine coordination complex of a chromium salt, such that 1-hexene is formed (US Patent No. 5,811,618).

The inventors are aware that some of the chromium-based processes for the trimerisation of ethylene are centred around catalyst systems which require the addition of a halogen in order to achieve the required selectivity and activity towards the formation of the desired products.

Summary of the Invention

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According to a first aspect of the invention there is provided a pyrrole ligand for an olefin oligomerisation catalyst system, the pyrrole ligand incorporating a halogen source.

25 In this specification, unless the context clearly indicates to the contrary, the term "pyrrole" refers to a hydrogen pyrrolide, i.e. C_4H_5N and the term "pyrrolide" is defined as a compound containing a 5-membered, nitrogen containing heterocycle. Derivatives of pyrrole may include substituted pyrrolides and/or any heteroleptic or homoleptic metal pyrrolide complexes or salts.

30

The ligand may be a halopyrrole or a derivative thereof.

The halopyrrole may be a halopyrrole-containing compound.

The halopyrrole-containing compound in the present invention may be any pyrrole derivative of the general formula, $X-(CH_2)_n-C_4H_4N$, where X can be a halide selected from the group consisting of fluoride, chloride, bromide and/or iodide, and n can be any number greater than 0.

Typical halopyrrole-containing compounds of the invention have from about 4 to about 20 carbon atoms per molecule.

The halopyrrole-containing compounds include derivatives of pyrrole having a bromoalkyl group bonded to the pyrrole ring. Catalyst systems including bromoalkyl pyrrole are believed to have enhanced activity and selectivity to a desired product(s).

Specific embodiments of the halopyrrole-containing compounds of the present invention include 2-(5'-bromopentyl) pyrrole, 2-(3'-bromopentyl) pyrrole and derivatives thereof.

The pyrrole containing compound can be either affirmatively added to the reaction, or generated in-situ.

Specific examples of halopyrrole-containing compounds include, but are not limited to hydrogen 2-(5'-bromopentyl) pyrrolide, sodium 2-(5'-bromopentyl) pyrrolide, lithium 2-(5'-bromopentyl) pyrrolide, potassium 2-(5'-bromopentyl) pyrrolide, cesium 2-(5'-bromopentyl) pyrrolide, chromium (III) 2-(5'-bromopentyl) pyrrolides, aluminium-diethyl-2-(5'-bromopentyl) pyrrolide, ethyl-aluminium-di-[2-(5'-bromopentyl)]pyrrolide, aluminium-tri-[2-(5'-bromopentyl)]pyrrolide, or the like.

The halogen source may be selected from the group consisting of fluoride, chloride, bromide and/or iodide.

The halogen source may be a salt or a compound including the halogen in a form available to the pyrrole for the formation of the halopyrrole.

The halogen source in the present invention may be any halogen derivative of
5 the general formula, $X-(CH_2)_n-X'$, wherein

- X may be a halide selected from the group consisting of fluoride, chloride, bromide and/or iodide;
- X' may be a halide selected from the group consisting of
10 fluoride, chloride, bromide and/or iodide or a good leaving group consisting of *p*-toluenesulfonyl and/or methylsulfonyl; and
- n may be any number greater than 0.

15 Specific examples of halogen-containing compounds useful as the halogen source include, but are not limited to, 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane, 1,6-dibromohexane, 1,7-dibromoheptane, 1,2-dichloroethane, 1,3-dichloropropane, 1,4-dichlorobutane, 1,5-dichloropentane, 1,6-dichlorohexane, 1,7-dichloroheptane, or the like.

20

According to a further aspect of the invention, there is provided a catalyst system for the oligomerisation of olefins, the catalyst system including:

- a chromium source;
- a metal alkyl; and
- 25 - a halopyrrole ligand substantially as described above.

The chromium source of said catalyst system may consist of one or more organic and/or inorganic chromium compounds having a chromium oxidation state ranging from 0 to 6.

30

These chromium compounds are suitably expressed by the general formula CrX_n , wherein

- X can be the same or different and represents an organic or inorganic radical, group or compound; and
- 5 - n is an integer from 0 to 6.

Examples of organic radicals can have from about 1 to 20 carbon atoms per radical.

- 10 The organic radicals may be selected from the group consisting of alkyl, alkoxy, ester, ketone and/or amido radicals.

Examples of organic compounds include, but are not limited to an amine compound, a phosphine compound, a phosphine oxide compound a nitrosyl group and/or an ether compound.

15

Examples of the inorganic radicals may include halides, nitrates and sulfates.

Specific examples of chromium sources include chromium (III) acetylacetonate, chromium (III) acetate, chromium (III) pyrrolides, chromium (III) 2,2,6,6-tetramethylheptadionate, chromium (III) tris(2-ethylhexanoate), bis(*N,N'*-bis(trimethylsilyl)benzamidinato) chromium (III) chloride, trichlorotris(4-isopropylpyridine) chromium (III), trichloro (*N,N,N',N',N''*-pentamethyldiethylenetriamine) chromium (III), chromium (III) chloride, bis-(2-dimethylphosphino-ethyl)ethylphosphine chromium (III), (2-dimethylphosphino-ethyl)(3-dimethylphosphinopropyl)methylphosphine chromium (III) chromium (III) naphthenate, chromium (II) acetate, chromium (II) pyrrolides, chromium (II) bis(2-ethylhexanoate) and/or chromium (II) chloride.

20

25

- 30 A metal alkyl may also be present in the catalyst system.

The metal alkyl of the catalyst system may be any heteroleptic or homoleptic metal alkyl compound.

One or more metal alkyls may be used in the catalyst system.

5

The alkyl ligand(s) may be any saturated aliphatic radical.

The alkyl ligand(s) on the metal can be aliphatic or aromatic.

10 The metal alkyl can have any number of carbon atoms, but preferably less than about 20 carbon atoms per molecule.

Examples of the afore-mentioned metal alkyl compounds include, but are not limited to, alkyl aluminium compounds, hydrolyzed alkyl aluminium compounds
15 (aluminoxanes), alkyl boron compounds, alkyl magnesium compounds, alkyl zinc compounds and/or alkyl lithium compounds.

The metal alkyl may be selected from an alkyl aluminium compound, a hydrolyzed alkyl aluminium compound and/or alkyl boron compound.

20

The metal alkyl may be an alkyl aluminium compound, expressed by the formula AlX_nR_{3-n} wherein

- n is an integer;
- R is an alkyl group; and
- 25 - X is a halogen atom.

The metal alkyl may be an alkyl aluminium compound, expressed by the formula R_nAlOR_{3-n} wherein

- n is an integer;
- 30 - R is an alkyl group; and
- X is a halogen atom.

It is believed that the use of said alkyl aluminium compound gives acceptable results in catalyst system activity and reduces the quantity of undesirable by-product polymer.

- 5 Specific alkyl aluminium compounds may include trimethyl aluminium, triethyl aluminium, tripropyl aluminium, tributyl aluminium, triisobutyl aluminium, diethyl aluminium chloride, diethyl aluminium bromide, diethyl aluminium ethoxide, ethyl aluminium dichloride, ethyl aluminium sesquichloride, or the like, and mixtures thereof.

10

The catalyst system may contain a hydrocarbon compound as solvent for the homogeneous catalyst system. The hydrocarbon compound can be any saturated or unsaturated aliphatic hydrocarbon compound.

- 15 The unsaturated hydrocarbon compound can have any number of carbon compounds per molecule, but usually contain less than 20 carbon atoms due to commercial availability and end use.

20 Examples of unsaturated hydrocarbon compounds include, but are not limited to ethylene, 1-hexene, 1,3-butadiene, 1,4-cyclo-octadiene, benzene, toluene, ethylbenzene, xylene, and the like.

Examples of saturated hydrocarbon compounds include, but are not limited to cyclohexane, hexane, heptane and the like.

25

The inventors believe that by incorporating the halogen source with the pyrrole ligand a process using a catalyst system including said halopyrrole has the advantage of decreasing the number of components needed to prepare the catalyst system without compromising the advantages associated with
30 homogeneous catalyst systems. Furthermore, the inventors believe that the

halopyrrole has the advantage of simplifying the catalyst system thereby making it easier and more efficient to prepare on an industrial scale.

According to yet a further aspect of the invention, it has been found that 1-hexene can be produced in a high selectivity and high yield by the trimerisation of ethylene using a catalyst system comprising a combination of at least a chromium source, a metal alkyl and a halopyrrole ligand.

Examples of Performing the Invention:

10

Preparation of 2-(5'-bromopentyl) pyrrole.

To a stirred solution of the pyrrole in dry diethyl ether under nitrogen was added a solution of BuMgBr (1.1 equivalents of a 1.0 M solution in diethyl ether) at 0°C and the resulting solution was stirred at 0°C. After a period of 1 hour a solution of 1,5-dibromopentane (2.0 equivalents) in dry diethyl ether was added to the reaction mixture using a syringe and the resulting reaction mixture was stirred at 0°C. After completion of the reaction, the reaction mixture was poured into a saturated NaHCO₃ solution, extracted with diethyl ether, dried over MgSO₄, and concentrated under reduced pressure. The resulting residue was purified using column chromatography on silica, eluting with hexane-ethyl acetate, to afford the title compound as a brown oil.

20

Example 1

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Ethylene trimerisation using 2-(5'-bromopentyl) pyrrole as both the ligand and halogen source.

All procedures were carried out under inert conditions, using pre-dried reagents

30

The catalyst system was prepared as follows: 0.06 mmol of chromium(III) ethylhexanoate was combined with 0.18 mmol of 2-(5'-bromopentyl) pyrrole and 1.2 mmol of triethylaluminium in 50 ml of dry cyclohexane. The catalyst complex was activated at room temperature for a period of two hours.

5

This solution, together with an additional 70 ml cyclohexane, was charged to a pressure reactor, fitted with a mechanical stirrer. The reactor temperature was maintained at 100 – 120 °C, while the ethylene pressure was kept at 35 bar. Thorough mixing was ensured by mixing speeds of 1100 RPM's. Thirty minutes later the reaction was terminated by the injection of 1-butanol into the pressure reactor. After releasing ethylene from the autoclave the by product polymers in the reaction were separated by filtration and the product/solvent phase was analysed by GC.

15 A catalyst activity of 17250 g product / g Cr / hour was observed. The selectivity towards C₆ products was 89.2 mass%, while the selectivity observed towards 1-hexene formation was 95.0 mass %. The polymeric side product obtained from the above reaction comprised less than 1 mass % of the reaction products.

20 **Example 2**

Ethylene trimerisation using 2-(3'-bromopropyl) pyrrole as both the ligand and halogen source.

25 The catalyst system was prepared as follows: 0.06 mmol of chromium(III) ethylhexanoate was combined with 0.18 mmol of 2-(3'-bromopropyl) pyrrole and 1.2 mmol of triethylaluminium in 50 ml of dry cyclohexane. The catalyst complex was activated at room temperature for a period of two hours.

30 This solution, together with an additional 70 ml cyclohexane, was charged to a pressure reactor, fitted with a mechanical stirrer. The reactor temperature was

maintained at 100 – 120 °C, while the ethylene pressure was kept at 35 bar. Thorough mixing was ensured by mixing speeds of 1100 RPM's. Thirty minutes later the reaction was terminated by the injection of 1-butanol into the pressure reactor. After releasing ethylene from the autoclave the by product polymers in
5 the reaction were separated by filtration and the product/solvent phase was analysed by GC.

A catalyst activity of 14866 g product / g Cr / hour was observed. The selectivity towards C₆ products was 86.0 mass%, while the selectivity observed towards 1-
10 hexene formation was 94.1 mass %. The polymeric side product obtained from the above reaction comprised less than 1 mass % of the reaction products.

Claims:

1. A pyrrole ligand for an olefin oligomerisation catalyst system, the pyrrole
5 ligand incorporating a halogen source.
2. A ligand as claimed in claim 1 wherein the ligand is a halopyrrole.
3. A ligand as claimed in claim 1 wherein the ligand is a derivative of a
10 halopyrrole.
4. A ligand as claimed in claim 2 or claim 3 wherein the halopyrrole is a
halopyrrole-containing compound.
- 15 5. A ligand as claimed in claim 4 wherein the halopyrrole-containing
compound is a pyrrole derivative of the general formula, $X-(CH_2)_n-C_4H_4N$, where
X is a halide selected from the group consisting of fluoride, chloride, bromide
and/or iodide, and n is any number greater than 0.
- 20 6. A ligand as claimed in claim 5 wherein the halopyrrole-containing
compound has from about 4 to about 20 carbon atoms per molecule.
7. A ligand as claimed in any one of claims 4 to 6 wherein the halopyrrole-
containing compound is a derivative of pyrrole having a bromoalkyl group bonded
25 to the pyrrole ring.
8. A ligand as claimed in any one of claims 4 to 6 wherein the halopyrrole-
containing compound is selected from the group including: hydrogen 2-(5'-
bromopentyl) pyrrolide, sodium 2-(5'-bromopentyl) pyrrolide, lithium 2-(5'-
30 bromopentyl) pyrrolide, potassium 2-(5'-bromopentyl) pyrrolide, cesium 2-(5'-
bromopentyl) pyrrolide, chromium (III) 2-(5'-bromopentyl) pyrrolides, aluminium-

diethyl-2-(5'-bromopentyl) pyrrolide, ethyl-aluminium-di-[2-(5'-bromopentyl)]pyrrolide, and aluminium-tri-[2-(5'-bromopentyl)]pyrrolide.

9. A ligand as claimed in any one of the preceding claims wherein the
5 halogen source is selected from the group consisting of fluoride, chloride, bromide and/or iodide.

10. A ligand as claimed in any one of claims 1 to 8 wherein the halogen
10 source is a salt or a compound including the halogen in a form available to the pyrrole for the formation of the halopyrrole.

11. A ligand as claimed in any one of claims 1 to 8 wherein the halogen source is a halogen derivative of the general formula, $X-(CH_2)_n-X'$, wherein:-

- 15 - X is a halide selected from the group consisting of fluoride, chloride, bromide and/or iodide;
- X' is a halide selected from the group consisting of fluoride, chloride, bromide and/or iodide or a good leaving group consisting of *p*-toluenesulfonyl and/or methylsulfonyl; and
- 20 - n is a number greater than 0.

12. A ligand as claimed in any one of claims 1 to 8 wherein the halogen source is selected from the group including: 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane, 1,6-dibromohexane,
25 1,7-dibromoheptane, 1,2-dichloroethane, 1,3-dichloropropane, 1,4-dichlorobutane, 1,5-dichloropentane, 1,6-dichlorohexane, and 1,7-dichloroheptane.

13. A catalyst system for the oligomerisation of olefins, the catalyst system
30 including:

- a chromium source;

- a metal alkyl; and
- a halopyrrole ligand substantially as claimed in any one of claims 1 to 12.

5 14. A catalyst system as claimed in claim 13 wherein the chromium source consists of one or more organic and/or inorganic chromium compounds having a chromium oxidation state ranging from 0 to 6.

15 15. A catalyst system as claimed in claim 14 wherein the chromium compounds are suitably expressed by the general formula CrX_n , wherein:-

- X can be the same or different and represents an organic or inorganic radical, group or compound; and
- n is an integer from 0 to 6.

15 16. A catalyst system as claimed in claim 15 wherein the organic radical can have from about 1 to 20 carbon atoms per radical.

17. A catalyst system as claimed in claim 15 or claim 16 wherein the organic radical is selected from the group including: alkyl, alkoxy, ester, ketone and/or amido radicals.

18. A catalyst system as claimed in claim 15 wherein the organic compound is selected from the group including: an amine compound, a phosphine compound, a phosphine oxide compound a nitrosyl group and/or an ether compound.

25 19. A catalyst system as claimed in claim 15 wherein the inorganic radical is selected from the group including halides, nitrates and sulfates.

20. A catalyst system as claimed in any one of claims 13 to 19 wherein the chromium source is selected from the group including: chromium (III) acetylacetonate, chromium (III) acetate, chromium (III) pyrrolides, chromium (III) 2,2,6,6-tetramethylheptadionate, chromium (III) tris(2-ethylhexanoate), bis(N,N'-

bis(trimethylsilyl)benzamidinato) chromium (III) chloride, trichlorotris(4-isopropylpyridine) chromium (III), trichloro (*N,N,N',N',N''*-pentamethyldiethylenetriamine) chromium (III), chromium (III) chloride, bis-(2-dimethylphosphino-ethyl)ethylphosphine chromium (III), (2-dimethylphosphino-ethyl)(3-dimethylphosphinopropyl)methylphosphine chromium (III) chromium (III) naphthenate, chromium (II) acetate, chromium (II) pyrrolides, chromium (II) bis(2-ethylhexanoate) and/or chromium (II) chloride.

21. A catalyst system as claimed in any one of claims 13 to 20 wherein the metal alkyl is a heteroleptic or homoleptic metal alkyl compound.

22. A catalyst system as claimed in any one of claims 13 to 21 wherein one or more metal alkyls are used in the catalyst system.

23. A catalyst system as claimed in any one of claims 13 to 22 wherein the alkyl ligand(s) on the metal is a saturated aliphatic radical.

24. A catalyst system as claimed in any one of claims 13 to 22 wherein the alkyl ligand(s) on the metal is aliphatic or aromatic.

25. A catalyst system as claimed in any one of claims 13 to 24 wherein the metal alkyl has less than about 20 carbon atoms per molecule.

26. A catalyst system as claimed in any one of claims 13 to 25 wherein the metal alkyl is an alkyl aluminium compound, expressed by the formula AlX_nR_{3-n} wherein:-

- n is an integer;
- R is an alkyl group; and
- X is a halogen atom.

27. A catalyst system as claimed in any one of claims 13 to 25 wherein the metal alkyl is an alkyl aluminium compound, expressed by the formula R_nAlOR_{3-n} wherein:-

- n is an integer;
- 5 - R is an alkyl group; and
- X is a halogen atom.

28. A catalyst system as claimed in any one of claims 13 to 27 wherein the metal alkyl is selected from the group including: alkyl aluminium compounds, hydrolyzed alkyl aluminium compounds (aluminoxanes), alkyl boron compounds, 10 alkyl magnesium compounds, alkyl zinc compounds and/or alkyl lithium compounds, trimethyl aluminium, triethyl aluminium, tripropyl aluminium, tributyl aluminium, triisobutyl aluminium, diethyl aluminium chloride, diethyl aluminium bromide, diethyl aluminium ethoxide, ethyl aluminium dichloride, ethyl aluminium sesquichloride, or the like, and mixtures thereof.

29. A catalyst system as claimed in any one of claims 13 to 27 wherein the catalyst system contains a hydrocarbon compound as solvent for the homogeneous catalyst system.

20

30. A catalyst system as claimed in claim 29 wherein the hydrocarbon compound is a saturated or unsaturated aliphatic hydrocarbon compound.

31. A catalyst system as claimed in claim 30 wherein the unsaturated hydrocarbon compound has less than 20 carbon atoms.

25

32. A catalyst system as claimed in any one of claims 29 to 31 wherein the unsaturated hydrocarbon compounds are selected from the group including: ethylene, 1-hexene, 1,3-butadiene, 1,4-cyclo-octadiene, benzene, toluene, ethylbenzene, and xylene.

30

33. A catalyst system as claimed in any one of claims 29 to 31 wherein the saturated hydrocarbon compounds are selected from the group including cyclohexane, hexane, and heptane.
- 5 34. A method of producing 1-hexene including at least the step of trimerising ethylene using a catalyst system comprising a combination of at least a chromium source, a metal alkyl and a halopyrrole ligand.
- 10 35. A method of producing 1-hexene as claimed in claim 34, wherein the halopyrrole ligand is prepared in situ in the ethylene reaction mixture.
36. A method of producing 1-hexene as claimed in claim 34, wherein the halopyrrole ligand is pre-prepared and introduced into the ethylene reaction mixture.
- 15 37. A pyrrole ligand for an olefin oligomerisation catalyst system according to the invention, as hereinbefore generally described.
- 20 38. A pyrrole ligand for an olefin oligomerisation catalyst system including any new and inventive integer or combination of integers, substantially as herein described.
- 25 39. A catalyst system according to the invention for the oligomerisation of olefins substantially as hereinbefore described or exemplified.
40. A catalyst system including any new and inventive integer or combination of integers, substantially as herein described.
- 30 41. A method according to the invention for producing 1-hexene, substantially as hereinbefore described or exemplified.

42. A method of producing 1-hexene including any new and inventive integer or combination of integers, substantially as herein described.

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